IR and UV spectroscopy of DNA Higher-Order Structures in the gas phase

F. Rosu, E. De Pauw, V. Gabelica
Department of Chemistry, University of Liège, B-4000 Liège, Belgium

R. Antoine, P. Dugourd
Laboratoire de Spectrométrie Ionique et Moléculaire, Lyon, France

DNA oligonucleotide complexes can be transferred from the solution to the gas phase using electrospray mass spectrometry (ESI-MS). In solution, hydrogen bonding and stacking interactions between nucleic bases are responsible of the formation of nucleic acid secondary structures. A longstanding question is whether the ions keep a folded conformation in the absence of solvent.

We will show that infrared (IR) and UV action spectroscopy provides useful information on the structure of nucleic acid ions in the gas phase. We also took up the challenge of using theoretical calculations of vibrational normal modes and electronic spectrum of large DNA polyanions to interpret the experimental spectra.

Before studying higher-order DNA structures (double helix, triplex, quadruplex and i-motif DNA), reference IR spectra of 6-mer single strands homobases (dG6, dA6, dC6 dT6) have been recorded using IRMPD spectroscopy. Reference spectra are useful to evaluate the contribution from each nucleobase (A, T, G, C) inside the complex. The wavelength range 1560-1760 cm^{-1} has been chosen according our previous works on IRMPD on G-quadruplex structures, which showed that C=O stretching of guanines was sensitive to the secondary structure.[1]

DNA polyanions trapped in a mass spectrometer undergo electron detachment following UV irradiation.[2] Photodetachment is a single-photon process and we will discuss whether the electronic spectra obtained via photodetachment can be used to probe gas phase nucleic acid ions structures. We made TDDFT calculations of nucleic acids polyanions to compare to the experimental spectra.

The UV spectra of double stranded DNA and G-quadruplex DNA structures in the gas phase show significant red-shift compared to the corresponding single strands. The change in the action spectra are related to the modification of the environment of the bases related to the formation of specific hydrogen bonds between the bases (Watson-Crick for the duplex and Hoogsteen for the quadruplex) and base stacking. TDDFT calculations of the electronic spectrum of different generated conformers show that the oligonucleotides spectra are modified upon structuration. This study demonstrates the use of UV spectroscopy to obtain signature of the biomolecule higher-order structure in the gas phase.

[1] V. Gabelica, F. Rosu, E. De Pauw, J. Lemaire, J.-C. Gillet, J.-C. Poully, F. Lecomte, G. Grégoire, J.P. Schermann, C. Desfrancois. *J.Am.Chem.Soc.* (2008), 130, 1810

[2] V. Gabelica, F. Rosu, T. Tabarin, C. Kinet, R. Antoine, M. Broyer, E. De Pauw, P. Dugourd. *J.Am.Chem.Soc.* (2007), 129, 4706